A discussion on producing agro-residue composites with isocyanate resins

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Abstract: With the urgent shortage of forest resource in China, using agro-residues as raw materials of composite become increasingly important. Agro-residue is the most potential fiber resource, which is helpful to sustainable development of composite industries in China. Based on a great deal of researches, this paper summarized and discussed some problems in using agro-residues as raw materials of composites, including raw material preparation, hot-pressing, bonding technology, preventing composite from going moldy. It is proposed that to manufacture the composite of rice straws or wheat straws, the isocayante resin is a suitable adhesive, and the appropriate technologies, bonding, and treatment measures are also needed.

Keywords: Agro-residue; Isocyanate resin; Composite; Problems existing

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Introduction

As a country of high deficiency in forestry resource, China has a forest volume of 11 270 million m^3, being in ranked 7^{th} in the world. The adoptable forest resource is 1 400-1 500 million m^3, which will only supply with wood for 5-6 years according to the present wood consumption. In 2000 the log output was 135 million m^3, about 60% of the requirement in China (Wang 1997). According to the prediction, the minimal need of wood is 200 million m^3 in 2000-2010 for China, with additional 77 million m^3 of firewood, which will make a gap of 60 million m^3 in the supply and demand of wood (Chen 2000). Nevertheless a higher demand of wood and the products is arisen with the development of construction and improvement of life standard.

In 1997, the production of composite was 16.48 million m^3 that coupled with great wood consumption and ecological environment damages (Zeng 2000). As a result, Chinese government issued some policies and started the Project of Nature Forest Protection to keep the forest resource sustainable development. It aggravates the wood conflicts of supply and demand. So, relying on only limited forest resource is not adapting to the new position of composite industry. And something must be done to make the sustainable development of composite industry in China, for instance, to adjust the structure of raw materials, to get new replaceable fiber resource, and to develop new products and new technologies.

As an agriculture country, China has abundant agro-residues and more than 20 kinds of residues could serve as raw materials for composite industry, for instance, the straws of rice and wheat, stalks of hemp, bean, and cotton. The total yield of agro-residues is more than 700 million t/a (Li 2000). If 3% of the yield were used, it could produce 21 million m^3 of composites, which equals 60 million m^3 of log, and could balance the wood margin of supply and demand in the 2010 of China. So, agro-residue was considered as the most potential substituting fiber resource of composite industry. However two thirds of agro-residue was burnt annually in China. The residue burning causes many problems, for instance, low visibility, polluting, disturbing the normal life, and so forth, which brings government's attention. Therefore, using agro-residues as raw materials of composite is not only a better way to mitigate the contradiction of wood supply and demand but also an efficient and comprehensive way of utilization, at meantime it can also reduce problems that was brought by the residue burning and increase farmer's income (Lu 1999). As a result, the technologies of agro-residue composite are researched and developed actively worldwide. It has become a driving tendency to manufacture non-wood composite in North America. In China many units have used these raw materials actively, for instance, Heilongjiang Province Academy of Forestry Science, Northeast Forestry Univ., Nanjing Forestry Univ., Tongji Univ., Jiangxi Research Institute of Building Composite.

Raw material preparing

Collecting and stocking

Of all Agro-residues, rice straws and wheat straws are the most abundant fiber resources. Based on the approximate estimation, the yield of paddy and wheat closes to that of straws. The yields of rice straws and wheat straws reach 360 million t and 200 million t, respectively, which

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account more than 70% of all straws and stalks. They are some materials used most difficulty in composite manufacturing. Therefore we are dedicating all along to the researching and developing of them.

Straws collecting and stocking come to be the first problem against the continuous production of composites for the seasonal supply and narrow distribution of agro-residues. Besides, the loose structure and the low piling density harden the problem. If the collecting area and production scale of mill were too large, freight of straws and the cost of straw composite would be increased. According to the result from the detailed survey and cost analysis (Hua *et al.* 2000), for a rather long time from now, the suitable production scale should be 15 000 m^3/a, and it could reach 30 000 m^3/a with the improvement of transportation. The natural piling density of straw, about 0.1-0.2 t/m^3, is quite low. After chipping or compressing, its density reaches 0.2-0.3 t/m^3 or 0.7-0.9 t/m^3 respectively. All these make transportation and stocking much easier. For a mill with a processing capacity of 15 000 t/a, it at least needs 100 000 m^3 of untreated straws, which covers a great area. Consequently it will follow some problems as moistureproofing, fireproofing, and mold proofing. However, some simple pre-treatment methods, such as cutting, chipping, and compressing, could solve those problems well. Then the treated straws can be transported to mill or storage dispersed or both. It is a better way as well to choose the mill site in an area with rich straw resources.

Dusting and dustproofing

For the sakes of loose structure, rich with lamina, dusts from field, and so on, a mass of dust could be brought in the refining process such as chopping, crashing, and flaking. The dusts do not only harm to the workers but to the environment and the residents nearby. Some measures are called for dealing with dusts: (i) to separate the vast dusting operations and advocate close producing; (ii) to increase properly the MC (moisture content) of straws before refining process; and (iii) to replace the flaking as kibbling which produces chips between flake/particle and coarse fiber for manufacturing fiberboard-like particleboard.

Hot-pressing technology

Hot-pressing temperature

Most straws and stalks are from annual graminaceous plants, meaning that shorter fiber length and high content of sugar, hot water extracts and carbohydrate with middle-to-low molecular weight. As a result, the hot-pressing temperature should be less than 150-160 °C, or pyrogenation will come with overheating, especially for long-time stocking straws and the fiberboard-like composite.

Moisture content

Using straws and stalks as raw materials of composite manufacturing, the moisture content (MC) of particles could be restrained greatly for the sakes of bad thermal conductance of mat, high content of thin-wall cell, and bad ventilation. Though isocyanate resin adapts to wide MC range, it is not suitable for the MC being more than 18%. When the MC is higher than 18%, glue failure will occur, such as blistering or delaminating, especially with higher density. In addition, the MC less than 4% is not suitable for isocyanate resin, for water being indispensable curing agent of isocyanate. Too low MC will produce great difference between board density and its nominal density, which may reduces the comprehensive performance significantly.

Density of composite

Although the density of straws and stalks is low, 0.2-0.3 t/m^3 of piling density, the compressing ratio is likely higher than that of wood composite with comparative performance. To keep necessary comprehensive performance, the common density of straw composite should not be less than 600 kg/m^3, while that of the rice straw composite is not less than 700 kg/m^3 even with the isocyanate resin.

Wax-based additive

Agro-residue contains quite much cutin and silicic compound, which are harmful to bonding. Some of waterproof materials can be added to improve the water-fast of composite. The wax could not improve the water-fast, but decrease the bonding strength. A little wax added has obvious effect on all performance of composite, but the effect of wax on the performance will not increase when adding more wax (Gu 2000). It means that wax-based additive to straw composite should be replaced by some other additives, for example, sodium chloride.

In addition, mold release is a problem when isocyanate serves as an adhesive that reacts to many materials. Wax-based release agent is widely used because of the good efficiency and low price. When release agent is superadded on caul plates after pre-pressing, no harm is done to composite performance. While it is mixed with adhesive in process of blending, the harm done to composite is quite similar to that of wax, and its effect depends on the amount of wax-based material added. Recently a new external release agent (YQT-W), with high efficiency and lower cost, was developed in Northeast Forestry University, which is water-borne and toxicant free with a cost about 300-450 RMB yuan/ t.

Adhesive and bonding technology

Urea-Formaldehyde (UF) resin is suitable for most agro-residue, such as hemp, hards, bagasse, and tobacco stalk, but it is not suitable for those as rice straw, rice shell, and wheat straw. When the resin consumption reaches 30% and the board density is near 850 kg/m^3, the performance of rice-straw composite cannot equal wood one (Qi 1992).

Table 1 showed that the ash content in straws is much

higher than that in wood, so is the silicon in ash. The extract by ether is mainly the waxiness, macroscopically the visible slick cuticle tissue. The wax layer and silicon form non-polar structure in cuticle of straws that prevent them from being wetted by adhesive and forming hydrogen bonding, which results in the lower strength of straw composite. Though we work hard with UF resin for manufacturing composite with rice straws and wheat straws, it is recognized that isocyanate resin is the most appropriate one. With utmost reactive isocyano group, strong and powerful chemical bonding will form high quality straw composite, but its high price prevents it from being widely used. Recently, two new prepolymer isocyanate resins, YQJ-A and YQJ-E, were developed in Northeast Forestry Univ. They have lower cost than resin alike, only 11 000-13 000 RMB yuan/t (including the tariff in China). When prepolymer isocyanate resin is used to manufacture wheat-straw composite, it has an equivalent product cost and similar composite performance to the UF one, meanwhile the former has a better bonding efficiency.

Table 1. Chemical components of 4 kinds of raw material

Material	Ash content (%)	Silicon over ash content (%)	Extracts by ether (%)	Extracts by 1%NaOH (%)
Rice straw	15.50	>60	0.65	47.70
Wheat straw	6.04	>65	0.51	44.56
Poplar	0.92	---	0.23	15.61
Larch	0.36	---	1.20	13.03

Another way to solve bonding problems of straws is pretreatment. Coupler or some reactive materials, H_2O_2 and NaOH for instance, can be adopted, which will form hydroxy functional group, or break the surface cutin, or improve the straw wetting. UF resin is applied with these pretreatments. The essence of increasing surface area is to break the surface cutin to a sense by machine and increase non-wax bonding surface. The process of kibbling and superadding NaOH may produce chips in shape between flake/particle and coarse fiber, which will make UF resin suitable to rice straws. To increase bonding surface by only polishing or rubbing, much dust will be produced.

Problems from going moldy

It is shown in Table 1 that the extracts from straws by 1% NaOH is 2-3 times as much as wood, meaning that straws and their composite will be moldy easily for higher content of carbohydrate with middle-to-low molecular weight. We discovered that the samples of rice-straw particleboard, discarding in shade and wet condition for weeks, overgrow with molds, which mainly are *Penicillium, Neurospora sitophila, Mucor, Rhizopus*, and few *Alternaria* (Gu *et al.* 2000). So some preservation measures should be taken to avoid raw material going moldy, for instance, waterproofing, dampproofing, better ventilation, and so on.

The prospects

The abundant, inexhaustible agro-residue is a mostly attractive raw material for composites in new age. With the development of composite market and increasingly shortage of wood resource, it is a better way to use non-wood materials for some composite mills. However there exist some problems, mainly on the performance and cost of straw composite. As the raw material of isocyanate resins is mass-produced and low-price prepolymer isocyanate resin develops, the cost of straw composite will decrease. In addition, the price of wood material will increase for policy intervention by government to protect forest resource, which will balance the disadvantage of high-price straw composites. It is estimated that the production of agro-residue composite will increasingly reach 30%-35% of total output of composite in 2010 (Wang 1998).

To conclude, it is of significance to take agro-residues as raw materials for composites and benefit agro-residue utilization, environment protection, nature forest protection, and sustainable development of composites industry.

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